

CATION DIFFUSION IN CARBONATE MINERALS: DETERMINING CLOSURE TEMPERATURES AND THE THERMAL HISTORY FOR THE ALH 84001 METEORITE. D. K. Fislser, R. T. Cygan, and H. R. Westrich, Geochemistry Department, Sandia National Laboratories, Albuquerque, NM 87185-0750

The diffusion rates of cations in carbonate minerals can be used to help constrain the thermal conditions expected for the formation and subsequent history of the ALH 84001 Martian meteorite. Since homogenization of the carbonate globules readily occurs at elevated temperatures—the extent being a function of grain size and diffusion coefficient for a given temperature—one can examine the measured compositional zoning patterns of the carbonate phases to see how the profiles might be preserved or modified [1-6]. Of course, thermal cooling histories of rocks can be quite complex and will need appropriate diffusion models in order to correctly interpret the compositional zoning patterns [7]. A convenient method based on the concept of closure temperature is provided by Dodson [8]. He derived an approximation for the relationship between cooling rate, grain size, and closure temperature for thermally-activated diffusion in geological systems. The diffusion-based cooling model is given by the following nonlinear equation:

$$\frac{E_a}{RT_c} = \ln \left(\frac{-ART_c^2 D_0}{a^2 E_a s} \right)$$

where E_a is the activation energy for diffusion, R is the gas constant, T_c is the closure temperature, D_0 is the diffusion coefficient, and A is a geometric factor (equal to 55 for a sphere), and s is the cooling rate. This equation provides a series of closure temperatures as a function of cooling rate and grain radius. The closure temperature represents that temperature below which a cation zoning pattern would be essentially frozen or preserved, as observed in the carbonate globules found in the Martian meteorite. The approximation includes the assumption that the system under consideration cools to a temperature low enough that diffusion is no longer significant over the life of the system.

Unfortunately, few data for the diffusion rates of cations in carbonate minerals are available that can be directly used to determine closure temperatures. However, our experimental approach that uses thin film-mineral diffusion couples [9] provides an accurate means of obtaining relatively low temperature diffusion data for cations. We have used a high-vacuum evaporator to deposit a thin film (~1000 Å) coating of an isotopically-enriched tracer onto a cleaved (104) calcite surface. The calcite

samples were then annealed in 1 atmosphere of CO_2 for 500 to 1000 hours and then analyzed using a Cameca IMS 4f ion microprobe. The resulting plot of tracer concentration (as $^{44}\text{Ca}/^{40}\text{Ca}$) versus analysis time is presented in Figure 1 and clearly shows the diffusion penetration.

The interface between the enriched coating and the mineral surface is identified by a discontinuity in the depth profile. The raw concentration profile is then transformed to concentration versus depth using a sputtering rate (2.85 Å/sec) determined by measuring the depth of a sputtered crater using a profilometer on an uncoated sample. The diffusion coefficient is obtained by fitting the final diffusion profile to an error function solution to Fick's diffusion equations, dependent on surface concentration C_s , bulk concentration C_b , and the diffusion coefficient D [10]. The variation of concentration as a function of depth x and experimental time t is described by:

$$C_x = C_s + (C_b - C_s) \operatorname{erf} \left(\frac{x}{4\sqrt{Dt}} \right)$$

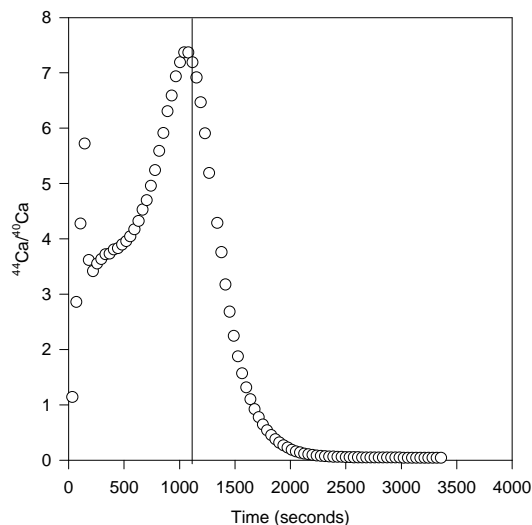


Figure 1. Raw ion microprobe profile as function of sputtering time for ^{44}Ca in calcite annealed at 650°C for 510 hours. The vertical line shows the location of the interface between the enriched coating and the calcite interface.

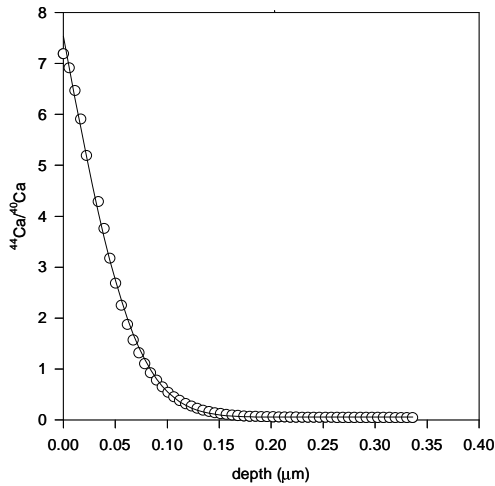


Figure 2. Diffusion profile for ^{44}Ca in calcite annealed at 650°C for 510 hours. The best fit (solid line) of the diffusion model to the observed data is based on the optimization of the C_b , C_s , and D parameters.

Figure 2 provides an example of the calcium diffusion profile from one of our preliminary experiments performed at 650°C for 510 hours. The profile exhibits the expected decrease of the calcium tracer (^{44}Ca) content up to a depth of approximately $0.15\ \mu\text{m}$. The best fit of the observed profile to the diffusion model given above is also shown in the figure, and provides a calcium self-diffusion coefficient of $1.1 \times 10^{-21}\ \text{m}^2/\text{sec}$.

Experiments were performed for calcium and magnesium diffusion in calcite at temperatures from $500^\circ - 700^\circ\text{C}$. Values for the activation energy E_a and pre-exponential term D_0 for the Arrhenius relation were obtained, and then used to calculate the expected closure temperatures for various grain sizes and cooling rates expected for the carbonate globules in the ALH 84001 meteorite.

Using the data for calcium diffusion in calcite [11], cooling rates must be more rapid than $1000^\circ/\text{my}$ for the cation zoning to have been preserved if the Martian carbonates formed at more than 650°C . Our preliminary experimental data indicate that magnesium diffusion rates in calcite ($D = 10^{-19}\ \text{m}^2/\text{s}$ at 700°C) are more than two orders-of-magnitude faster than those for calcium. The closure temperatures based on the magnesium diffusion data are lower and therefore require a more rapid cooling rate than those calculated based on the calcium diffusion data (see Figure 3). This analysis demonstrates that any model for the high temperature

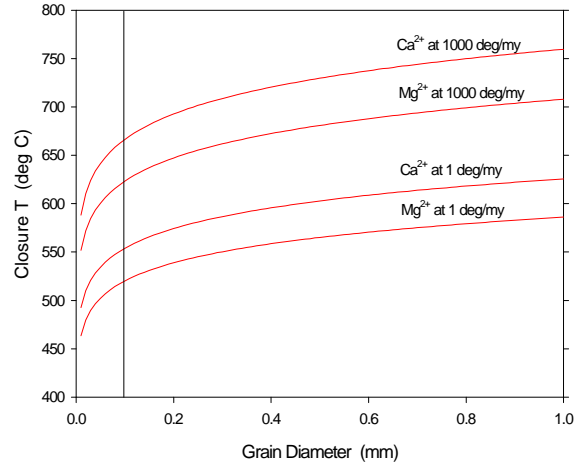


Figure 3. Closure temperatures as a function of grain diameter and cooling rate calculated for calcium and magnesium diffusion in calcite. The vertical line represents the mean diameter of the carbonate globules in the ALH 84001 meteorite.

formation of the carbonate assemblage requires rapid cooling for the preservation of the observed chemical zoning. However, a low temperature model for formation is not constrained by the experimental diffusion data.

References: [1] Harvey, R. and McSween, H. Y. (1996) *Nature*, 382, 49-51. [2] Mittlefeldt, D. W. (1994), *Meteoritics*, 29, 214-221. [3] Treiman, A. H. (1995), *Meteoritics*, 30, 294-302. [4] Thomas-Keprta, K. L. *et al.* (1997), *LPSC*, in press. [5] McKay, D. S., *et al.* (1996). *Science*, 273, 924-930. [6] Romanek, C. S., *et al.* (1994), *Nature*, 372, 655-657. [7] Ganguly, J. and Tazzoli, V. (1994), *Geoch. Cosmoch. Acta*, 58, 2711-2723. [8] Dodson, M. H. (1973), *Contrib. Min. Pet.*, 40, 259-274. [9] Schwandt, C. S. *et al.* (1993), *Pure Applied Geoph.*, 103, 631-642. [10] Crank, J. (1975) *The Mathematics of Diffusion*, Oxford University Press, London. [11] Farver, J. R. and Yund, R. A. (1996) *Contrib. Min. Pet.*, 123, 77-91.

Acknowledgments: We are grateful for the technical discussions with Kathie Thomas-Keprta and Craig Schwandt that led to the application of our experimental diffusion data to the Martian meteorite. This research was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Geosciences Research, under contract DE-AC04-94AL85000 with Sandia National Laboratories.